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| 13. SUPPLEMENTARY NOTES Dr. Michael R. Berman, Program Director | | | | | |
| 14. ABSTRACT Gas-liquid scattering experiments were used to investigate the uptake of HCl and HBr, the evaporation of water, and the hydrolysis of N ₂ O ₅ in sulfuric acid coated with the soluble surfactants n-butanol and n-hexanol under atmospheric conditions. The experiments show that HCl and HBr uptake is enhanced by butanol and hexanol films, water evaporation is unimpeded, and N ₂ O ₅ hydrolysis is reduced by twofold. This reduction likely occurs because N ₂ O ₅ is a large molecule whose transport is impeded by the butyl and hexyl chains covering the acid surface. In contrast, HCl and HBr uptake is enhanced because they are smaller molecules that penetrate through the alkyl chains and dissociate by protonating the OH groups of interfacial butanol and hexanol molecules. The hydrolysis of N ₂ O ₅ is the most important heterogeneous reaction in the atmosphere governing the depletion of ozone. The results suggest that this hydrolysis is overestimated in regions of the upper troposphere where small organic surfactants are present in high enough concentration to coat the surface of sulfuric acid aerosols. | | | | | |
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Final Technical Report for AFOSR Grant F49620-03-1-0045

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AFOSR Grant/Contract Information

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Objectives and Accomplishments

This technical report summarizes our studies of reactions of the atmospheric gases HCl, HBr, H₂O, and N₂O₅ with bare and surfactant-coated supercooled sulfuric acid.

Our objective is to develop a microscopic description of collisions and reactions of atmospheric gases with sulfuric acid aerosols that are responsible for altering the levels of ozone, N₂O₅, and halogen-containing gases in the atmosphere. In this grant period, we have extended our molecular beam studies of reactions of HCl and HBr with sulfuric acid to the even richer chemistry that occurs when aqueous solutions are coated with organic surfactants. This research is motivated by discoveries from aerosol field measurements that aqueous droplets in the upper troposphere contain significant quantities of organic molecules. These molecules typically incorporate functional groups that make them surface active, creating coatings that may impede gas uptake and alter the rates of chemical reactions that occur near the surface and in the bulk of sulfuric acid droplets. Thus, these films may act as barriers to gas uptake that would reduce gas-liquid reactions and suppress ozone depleting processes.

Over the past three years, we have investigated reactions of gaseous HCl, HBr, H₂O, and N₂O₅ with surfactant coatings on 56 to 68 wt % sulfuric acid at -60 °C, which are typical acid

concentrations and temperatures of the upper troposphere and lower stratosphere at middle latitudes. These three gases are among the most important in the atmosphere with respect to ozone depletion. The halogen-containing gases HCl and HBr dissolve in sulfuric acid, and react with other species such as HOCl (HOBr) and ClONO₂ (BrONO₂) to produce Cl₂ and Br₂. These gases breakup apart in sunlight to Cl and Br atoms, which efficiently catalyze the destruction of ozone in a two step reaction: $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$ and $\text{ClO} + \text{O}_3 \rightarrow \text{Cl} + 2\text{O}_2$. Thus, sulfuric acid aerosols “recycle” HCl and HBr, which are benign, into ozone depleting gases.

The key step that turns off the catalytic chlorine cycle is the “theft” of ClO by NO₂ to form the unreactive, reservoir species ClONO₂. The intermediate NO₂ is in turn supplied during the day by ambient N₂O₅, which breaks apart under sunlight into NO₂ and NO₃. How do sulfuric acid aerosols influence this reservoir reaction? These aerosols are a sink for N₂O₅, readily converting it into nitric acid through the reaction $\text{N}_2\text{O}_5 + 2\text{H}_2\text{O} \rightarrow 2\text{HNO}_3$. The hydrolysis of N₂O₅ is by far the most important heterogeneous in the atmosphere: globally, it is responsible for reducing ozone levels by 5% and NO and NO₂ levels by 40%.

Our studies show that coatings of short-chain alcohols on sulfuric acid alter the uptake of H₂O, HCl, and HBr and the hydrolysis of N₂O₅ in ways that were completely unexpected. We found that H₂O transport was unaffected by films of butanol and hexanol, that HCl and HBr uptake into the acid was enhanced rather than impeded, and that N₂O₅ hydrolysis was cut in half. These results are summarized below.

These studies have potentially significant implications for organic pollutants that rise through the atmosphere toward the tropopause and dissolve in aqueous droplets: small, surface-active organic molecules do not impede ozone depleting reactions involving HCl and HBr, but they do impede N₂O₅ hydrolysis, and therefore may reduce ozone depletion in particularly dirty regions of the atmosphere where the surfactant coverage will be high. Ongoing field measurements will hopefully soon assess the concentrations of organic molecules above the lower troposphere, and allow us to determine more precisely the effects of surfactants on sulfuric acid-mediated reactions.

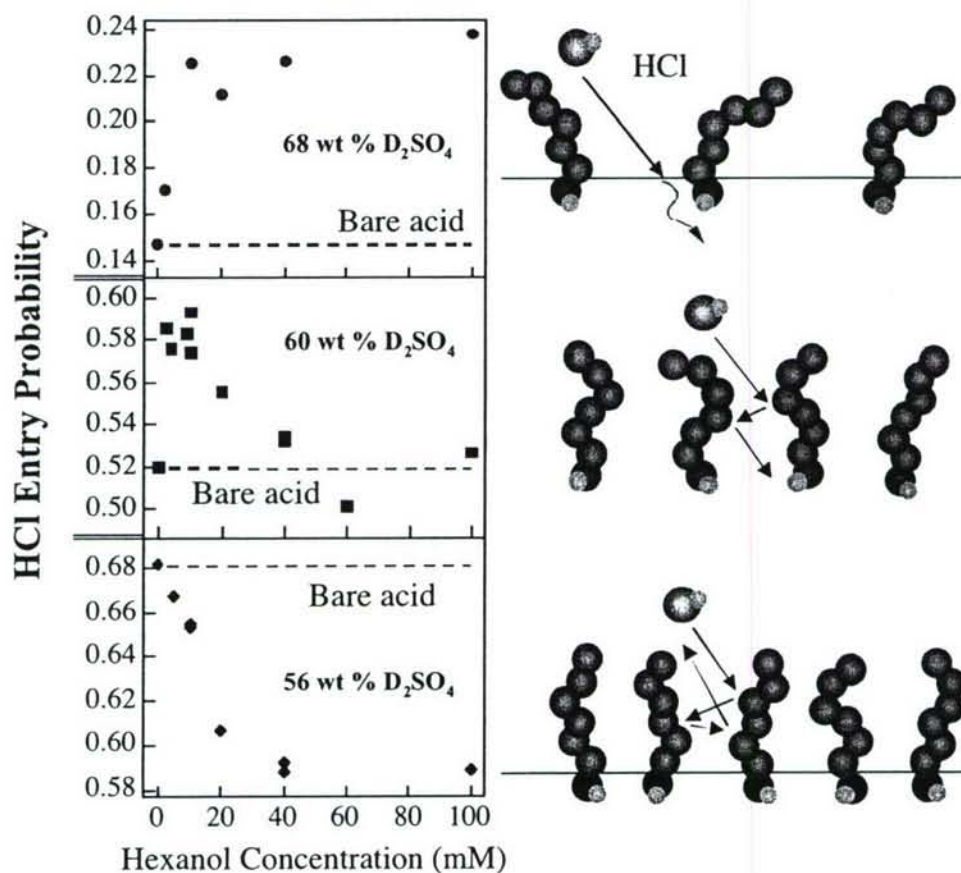
Specific Accomplishments

Our research shows that:

- 1) Short-chain organic molecules spontaneously segregate to the surface of cold sulfuric acid. Butanol, for example, coats the acid with a surface coverage equal to 50% of maximum packing (all chains upright and close-packed) on 60 wt % sulfuric acid at -60 °C, while the longer hexyl chains pack more tightly, reaching 66% maximum coverage. The chains do not pack tightly at 100% coverage even at saturation because of charge repulsion among the protonated ROH head groups, which pushes the chains apart.
- 2) Longer chain alcohols such as hexadecanol (16 carbon atoms) form compact monolayers on water at 25 °C, but do not coalesce well on the surface of sulfuric acid at -60 °C. Instead, they precipitate as solids. This finding is important because it implies that most soap-like molecules investigated so thoroughly at room temperature will not be good surfactants at the cold temperatures of the upper troposphere or stratosphere.
- 3) Water evaporation from 56 to 68 wt % sulfuric acid remains unchanged by the presence of a saturated butanol film. This remarkable result indicates that the butanol film is too porous to impede water transport through submonolayer film. This result implies that the condensation of water will also be unimpeded by the presence of butanol. We therefore predict that short-chain surfactants will not effect the growth or evaporation of aqueous acid aerosols in the atmosphere. This rule is broken when hexanol is spread on sulfuric acid, but only at concentrations below 54 wt % acid, where the evaporation of water is impeded by 20%.
- 4) The uptake of HCl and HBr into sulfuric acid aerosols is enhanced by the presence of butanol films. This result surprised us completely. Our experiments indicate that, like water, HCl and HBr readily pass through holes in the porous butanol film, where they reach an aqueous surface rich in OH groups from the alcohols themselves. On bare sulfuric acid, HCl and HBr most likely enter the acid by protonating H₂O molecules at the surface of the acid and dissolving as H⁺ and Cl⁻. On alcohol-coated acid, the alcohol OH groups provide extra protonation sites for HCl and HBr. Instead of impeding HCl and HBr transport, the alcohol

surfactants “tease” HCl and HBr into the acid medium through acid- base reactions.

- 5) In contrast to butanol, hexanol coatings enhance or impede the entry of HCl into sulfuric acid in ways that depend sensitively on the concentration of sulfuric acid, as shown in the figure below. For 70 wt % D_2SO_4 , the alcohol groups are sufficiently protonated that the maximum coverage reaches only 62% of a compact monolayer. This film behaves like butanol and enhances HCl entry into the acid. As the acid concentration is lowered to 60 wt % D_2SO_4 , the entry at first rises at low hexanol coverage and then drops back to the bare acid value as the film becomes more compact. Finally, hexanol films on 56 wt % acid actually impede HCl entry, most likely because the film density increases to 68% of a monolayer. We imagine that at lower acid concentrations, HCl transport will be impeded even more effectively.



- 6) The hydrolysis of N_2O_5 is suppressed by butanol and hexanol films in 72 wt % H_2SO_4 at -60°C , which reduce the hydrolysis rate from 15% on bare acid to 10% on butanol-coated acid and 6% on hexanol-coated acid. The studies suggest that N_2O_5 is either too big to move easily through films permeable to HCl and HBr, or that the alcohol OH groups dilute the acid region and suppress reaction between N_2O_5 and H_3O^+ or H_2O . It is at present difficult to assess the importance of these measured reductions: in polluted areas where surfactants are plentiful, it has been postulated that the effect of surfactants on N_2O_5 hydrolysis may have a strong impact on regional air quality (see Brown et al, *Science*, **311**, 67 (2006)).

Personnel Supported by AFSOR During the Grant Period

Principal Investigator

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The PI is directly supported by AFOSR for one month each year during the summer.

Graduate Students

Jennifer Splan Lawrence completed her Ph. D. under this grant and graduated in May, 2004. She is the first author on two publications listed below exploring water evaporation and HCl and HBr entry into butanol-coated sulfuric acid. Jennifer is presently teaching chemistry at Grand Valley State College.

Samuel Glass completed his Ph. D. under this grant and graduated in July, 2005. Sam was responsible for our studies of water evaporation and HCl and HBr entry into hexanol-coated sulfuric acid, including studies showing that evaporation and uptake depend sensitively on acid concentration. Sam is presently a research scientist at the Forest Products Research Laboratory in Madison, WI applying his knowledge of chemistry to the role of humidity in wood.

Undergraduate Students

James Krier has played a key role in our studies by measuring the surface tensions of organic molecules on the surfaces of sulfuric acid. He is presently writing a manuscript on this work, which has already been used in our publications and has influenced other studies, including those carried out by John Hemminger and Heather Allen. Jim will intends to enroll in graduate school in chemistry upon graduation.

Post-Doctoral Fellows

Seong-Chan Park was initially supported by prestigious Korean Fellowship and Dreyfus Environmental Postdoctoral Fellowships, and was then supported by AFOSR for his last four months in Madison. Seong-Chan single handedly measured the rates of N_2O_5 hydrolysis in butanol-coated and hexanol-coated sulfuric acid. These were probably the most difficult experiments we have every undertaken. He is presently a postdoctoral fellow in Korea and will apply for faculty positions this fall.

Publications during this Grant Period

The Evaporation of Water through Butanol Films at the Surface of Supercooled Sulfuric Acid, Jennifer R. Lawrence, Samuel V. Glass, and Gilbert M. Nathanson, *Journal of Physical Chemistry A*, **109**, 7449 (2005).

This article established that molecular beam scattering experiments can be applied to studies of surfactant coatings on aqueous surfaces in vacuum. We showed that argon atom scattering, coupled with surface tension measurements, can be used to quantitatively characterize surfactant films in vacuum. We also demonstrated that water evaporation is unimpeded by butanol films on 60-68 wt % D_2SO_4 , implying that short-chain surfactants form films that are too porous to suppress the growth or shrinkage of sulfuric acid droplets.

Surfactant Control of Gas Uptake: The Effects of Butanol on HCl Entry into Supercooled Sulfuric Acid, Jennifer R. Lawrence, Samuel V. Glass, and Gilbert M. Nathanson, *Journal of*

Physical Chemistry A, 109, 7458 (2005)

The article shows that butanol films on 60-68 wt % D_2SO_4 does not impede the transport of HCl or HBr into the acid, and instead actually enhance entry, for example, by a factor of two (from 14% to 27%) on 68 wt % acid. This startling finding suggests that the OH groups of the alcohol provide extra interfacial protonation sites that assist the dissociation of HCl and HBr into H^+ , Cl^- , and Br^- , which then dissolve in the acid.

Evaporation of Water and Uptake of HCl and HBr through Hexanol Films at the Surface of Supercooled Sulfuric Acid, Samuel V. Glass, Seong-Chan Park, and Gilbert M. Nathanson, *Journal of Physical Chemistry A*, **110**, 7593 (2006).

Hexanol molecules form films on sulfuric acid that act as barriers or catalysts for the entry of HCl and HBr, depending on acid and hexanol concentration, as shown in the figure above. This publication demonstrates that the barrier properties of an organic film can be controlled not only by chain length and surfactant coverage, but also by the nature of the underlying subphase.

The Inhibition of N_2O_5 Hydrolysis in Sulfuric Acid by 1-Butanol and 1-Hexanol Surfactant Coatings, Seong-Chan Park, Daniel K. Burden, and Gilbert M. Nathanson, *Journal of Physical Chemistry A*, **111**, 2921, 2007.

The hydrolysis of N_2O_5 by aqueous aerosols is the most important heterogeneous reaction in the atmosphere, responsible for reducing NO and NO_2 levels by 40% and ozone by 5%. Our studies show that butanol and hexanol films on 72 wt % H_2SO_4 reduce hydrolysis from 0.15 on the bare acid to 0.10 and 0.06 for the butanol and hexanol-coated acids, respectively. These reductions are significant, but are likely to be reached only in highly polluted areas.